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Electronic Structures of Pyridine N-Oxide and 4-Nitrosopyridine N-Oxide

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The π-electron structure of pyridine N-oxide was calculated by the Pariser-Parr-Pople method, the effect of σ-polarization of the $N \rightarrow O$ bond upon the valence state ionization potentials and electron affinities being taken into account. By the aid of these results, the π-electron structure of 4-nitrosopyridine N-oxide was studied by the composite system method. The calculated transition energies and oscillator strengths can satisfactorily explain the observed electronic absorption spectrum. The 372 mμ band was ascribed to the charge-transfer transition from the oxygen atom of the $N \rightarrow O$ group to the nitroso group via the pyridine nucleus.

Introduction

It is known that amine N-oxide molecules frequently show characteristic features in physicochemical and spectroscopic observations [10]. In the present study, we carried out the SCF MO CI calculation on the π-electron structure of pyridine N-oxide, and thereafter, the π-electron structure of 4-nitrosopyridine N-oxide was investigated by the composite system method. The observed electronic absorption spectra were compared with the calculated transition energies and oscillator strengths.

Theoretical

The π-electron structure of pyridine N-oxide was calculated by the Pariser-Parr-Pople method [11], the two-center Coulomb repulsion integrals being estimated by the Nishimoto-Mataga approximation [9].

The σ-core polarization in the $N \rightarrow O$ bond of pyridine N-oxide is very large, so that the valence state ionization potentials and electron affinities of $2p\pi$ AO's of oxygen and nitrogen may deviate considerably from the values of free atoms [2]. The valence state energies of these atoms can be represented in a good approximation by the quadratic equation of the extent of charge transfer (δ) in the σ core from the nitrogen atom to the oxygen atom [12].

$$\begin{aligned}
I_{\mathrm{O1}}(s^2x^2yz^2 \rightarrow s^2x^2yz) &= 14.89 - 20.25\delta + 7.47\delta^2 \\
I_{\mathrm{O2}}(s^2x^2yz \rightarrow s^2x^2y) &= 37.93 - 25.04\delta + 4.17\delta^2 \\
(\mathrm{O}^{-\delta}\mathrm{O}^{-\delta}|\mathrm{O}^{-\delta}\mathrm{O}^{-\delta})_{\mathrm{O}} = I_{\mathrm{O2}} - I_{\mathrm{O1}} &= 23.04 - 4.79\delta - 3.30\delta^2 \\
I_{\mathrm{N1}}(t_1^{2-\delta}t_2t_3z \rightarrow t_1^{2-\delta}t_2t_3) &= 14.51 + 12.81\delta + 1.555\delta^2 \\
A_{\mathrm{N}}(t_1^{2-\delta}t_2t_3z \rightarrow t_1^{2-\delta}t_2t_3z^2) &= 1.20 + 6.73\delta + 4.315\delta^2 \\
(\mathrm{N}^{+\delta}\mathrm{N}^{+\delta}|\mathrm{N}^{+\delta}\mathrm{N}^{+\delta})_{\mathrm{N}} = I_{\mathrm{N1}} - A_{\mathrm{N}} &= 13.31 + 6.08\delta - 2.76\delta^2 \quad (\mathrm{eV})
\end{aligned}$$

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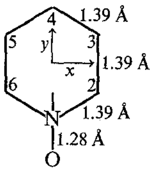
Table 1. *Molecular orbitals and orbital energies of pyridine N-oxide for the case of* $\delta = 0.70$ *and* $\beta_{N \to O} = -2.00$ eV

MO(φ_i)	Orbital energy (eV)	C_{i1}	C_{i2}	C_{i3}	C_{i4}	C_{i7}
$\varphi_1(b_2)$	−16.1672	0.7449	0.3699	0.1851	0.1312	0.2927
$\varphi_2(b_2)$	−12.6765	−0.3084	0.0927	0.4602	0.6095	−0.3044
$\varphi_3(a_2)$	−11.1922	0.0	−0.5050	−0.4950	0.0	0.0
$\varphi_4(b_2)$	− 9.4012	−0.1392	−0.2868	0.0777	0.3182	0.8384
$\varphi_5(b_2)$	− 2.1388	0.4879	−0.3427	−0.2411	0.5555	−0.3196
$\varphi_6(a_2)$	− 1.7786	0.0	−0.4950	0.5050	0.0	0.0
$\varphi_7(b_2)$	1.0357	−0.3042	0.3935	−0.4357	0.4488	0.1292



In order to estimate δ, we consider the trimethylamine N-oxide molecule which consists of a σ-electron donor part (trimethylamine) and a σ-electron acceptor part (the oxygen atom). By the aid of the dipole moment of this molecule [8] and of the lone pair moment (0.92*D*) of the sp^3 hybridized nitrogen atom, we estimated to be $\delta = 0.71$ for the oxygen valence AO without hybridization.

In pyridine N-oxide the hybridization of nitrogen atom changes to sp^2 from sp^3 in trimethylamine N-oxide. However, δ is shown to be insensitive to the hybridization. Thus, we assume that the δ value of pyridine N-oxide is in the range of $0.60 \sim 0.70$.

The core resonance integrals β_{CC} and β_{CN} between the adjacent atoms in the ring were assumed to be equal to those given by Pariser-Parr i.e. $\beta_{CC} = -2.370$ eV and $\beta_{CN} = -2.576$ eV [11]. The core resonance integral between the nitrogen and oxygen atoms of the N → O bond ($\beta_{N \to O}$) was taken as a parameter and chosen so as to give the best coincidence between the observed transition energies and the theoretical ones which were calculated by considering the configuration interaction among all the singly excited configurations. The results of the SCF calculation and of the configuration interaction calculation are summarized in Tables 1 and 2, respectively[1].

The π-electron structure of 4-nitrosopyridine N-oxide was calculated by the composite system method[2], nine lower singly excited configurations of pyridine N-oxide[3] and the two charge-transfer configurations corresponding to the electron transfer from the highest and second highest occupied orbitals of pyridine N-oxide (φ_4 and φ_3 in Table 1, respectively) to the vacant orbital of the nitroso group. The

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[1] The actual calculations have been carried out by an electronic computer Okitac 5090H located in our Institute. The authors wish to express their sincere thanks to Dr. Ichiro Hanazaki of our Institute for his kindness in permitting them to use the computer program written by him.

[2] The similar calculation has been made for nitrosobenzene [13].

[3] The energies of these configurations were evaluated by adding small corrections due to the electrostatic interaction with the nitroso group to the excitation energies of pyridine N-oxide given in Table 2.

energy difference between these two charge-transfer configurations was calculated to be

$$H_{CT_4,CT_4} - H_{CT_3,CT_3} = -1.346\ \text{eV}.$$

The absolute energy of one of the two charge-transfer configurations was decided to give the best coincidence between the observed and calculated transition energies.

Results and Discussion

The calculated transition energies and oscillator strengths of pyridine N-oxide are given in Table 2 in comparison with the observed values. The 281 mμ band may safely be assigned to the $W_0 \rightarrow W_2$ transition. The $W_0 \rightarrow W_1$ transition band is expected to appear close to the $W_0 \rightarrow W_2$ transition band. According to the present calculation, either of them was found to have the character of the intramolecular charge-transfer band. The existence of the two $\pi \rightarrow \pi^*$ transition bands in this wavelength region was supported by the recent SCF MO calculations made by Bene and Jaffe [1] and also by Evleth [3], which appeared in the literatures after our first paper was read [5]. Our result seems to be in better agreement with observed transition energies and oscillator strengths than the results by the other authors. Kubota *et al.* [14] also obtained the similar conclusion.

The analysis of the observed dipole moment of pyridine N-oxide shows that the π moment in the ground state of this molecule is $0.78D$ with the negative end in the pyridine nucleus [4, 7]. The theoretical value is $0.84D$ in the case of $\delta = 0.70$ and $0.33D$ in the case of $\delta = 0.60$ in the same direction. The π moment in W_2 state of pyridine N-oxide was calculated to be $7.68D$ with the negative end in the pyridine nucleus. When the σ moment of pyridine N-oxide is estimated to be $-5.01D$, the total dipole moment in the W_2 state amounts to $2.66D$, which is considerably smaller than the value in the ground state $(-4.20D)$. This is in accordance with the prediction based on the observed solvent shift [6].

As is shown in Fig. 1, 4-nitrosopyridine N-oxide exhibits two bands at $\lambda_{max} = 372$ mμ$(f = 0.274)$ and $\lambda_{max} = 258$ mμ$(f = 0.172)$ in *n*-heptane. They shift to shorter wavelengths by the increase in the solvent polarity in accordance with

Table 2. *The calculated and observed transition energies* (ΔE) *and oscillator strengths* (f) *of pyridine* N-*oxide for the case of* $\delta = 0.70$ *and* $\beta_{N\rightarrow O} = -2.00$ eV

	$\Delta E_{calc.}$(eV)	$\Delta E_{obs.}$(eV)[b]	$f_{calc.}$	$f_{obs.}$[b]	Direction of transition moment
$W_0 \rightarrow W_1$	3.87	3.81	0.019	0.016	x
$W_0 \rightarrow W_2$	4.47	4.40	0.457	0.205	y
$W_0 \rightarrow W_3$	5.55[a]	5.72	0.342	0.196	x
$W_0 \rightarrow W_4$	6.35[a]	6.60	0.399	0.246	y
$W_0 \rightarrow W_5$	6.89		0.001		y
$W_0 \rightarrow W_6$	7.39		0.543		y
$W_0 \rightarrow W_7$	7.41		0.605		x

[a] The $W_0 \rightarrow W_3$ and $W_0 \rightarrow W_4$ transition bands are known to correspond to the ${}^1L_b$ and ${}^1L_a$ bands of pyridine, respectively.

[b] Yamakawa, M., T. Kubota, and H. Akazawa: To be published in Spectrochim. Acta.

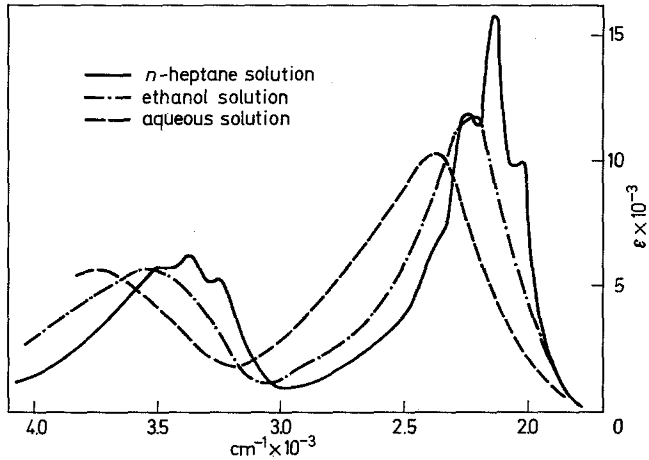

Fig. 1. The ultraviolet absorption spectra of 4-nitrosopyridine N-oxide in n-heptane, ethanol and aqueous solutions. The measurements were made with a Cary recording spectrophotometer Model 14

the general tendency of aromatic N-oxides. The observed bands are assigned in Table 3 by comparing with the theoretical results. It may be noticed that the 372 mμ band may be characterized as a charge-transfer band from the oxygen atom of the N→O group to the nitroso group via the pyridine nucleus, and that the 258 mμ band may have a mixed character of the local excitation of the pyridine nucleus and of the charge-transfer excitation from the pyridine nucleus to the nitroso group.

Table 3. *Observed and calculated transition energies (ΔE) and oscillator strengths (f) of 4-nitrosopyridine* N-*oxide*[a]

	$\Delta E_{calc.}$(eV)	$\Delta E_{obs.}$(eV)	$f_{calc.}$	$f_{obs.}$
$W_0' \to W_1'$	3.60	3.27	0.491	0.275
$W_0' \to W_2'$	3.81	covered by the $W_0' \to W_1'$ band	0.014	
$W_0' \to W_3'$	4.94	4.81	0.140	0.172
$W_0' \to W_4'$	5.44	covered by the $W_0' \to W_3'$ band	0.006	
$W_0' \to W_5'$	6.70		0.085	
$W_0' \to W_6'$	6.84		0.448	

[a] In this calculation, β_{CN} was taken to be -2.50 eV [Nagakura, S., M. Kojima, and Y. Maruyama: J. molecular Spectroscopy **13**, 174 (1964)].

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